

FACILE CREATION OF SUPEROLEOPHOBIC- SUPERHYDROPHILIC AND SUPEROLEOPHILIC- SUPERHYDROPHOBIC SURFACES BY USING FLUOROALKYL- END-CAPPED VINYLTRIMETHOXYSILANE OLIGOMERIC NANOCOMPOSITES

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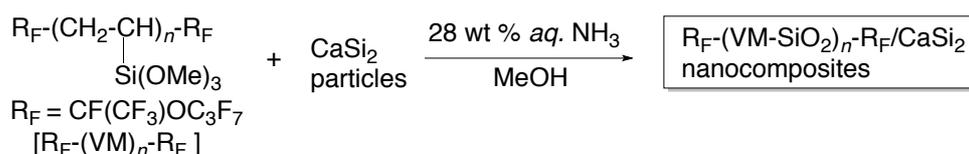
Summary: *Fluoroalkyl end-capped vinyltrimethoxysilane oligomer/calcium silicide nanocomposites $[R_F-(VM-SiO_2)_n-R_F/CaSi_2]$; $R_F = CF(CF_3)OC_3F_7$ have been prepared by the sol-gel reactions of the corresponding fluorinated oligomer $[R_F-(CH_2-CHSi(OMe)_3)_n-R_F]$; $n = 2, 3$; $R_F-(VM)_n-R_F]$ with calcium silicide particles under alkaline conditions. $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites, in which the contents of $CaSi_2$ are 1 ~ 8 %, can give the superhydrophobic and highly oleophobic characteristics on the modified glass surfaces. In contrast, $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites, in which the contents of $CaSi_2$ are 67 ~ 88 %, enabled the modified surfaces to give the superoleophobic-superhydrophilic characteristic. Similarly, $R_F-(VM)_n-R_F$ oligomer can undergo the sol-gel reaction in the presence of talc particles under alkaline conditions at room temperature to give the corresponding fluorinated oligomeric silica/talc nanocomposites $[R_F-(VM-SiO_2)_n-R_F/Talc]$. A variety of guest molecules such as 2-hydroxy-4-methoxybenzophenone (HMB) and bisphenol A (BPA) are effectively encapsulated into the $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposite cores to afford the corresponding fluorinated nanocomposites-encapsulated these guest molecules. The nanocomposites thus obtained are applicable to the surface modification of glass to afford the superoleophilic-superhydrophobic characteristic on the modified surface.*

1 INTRODUCTION

During our comprehensive studies on the nanocomposite reactions of partially fluoroalkylated polymers, such as fluoroalkyl end-capped oligomers with the inorganic materials [1 ~ 8], we have already found that fluoroalkyl end-capped vinyltrimethoxysilane oligomer [$R_F-(CH_2CHSi(OMe)_3)_n-R_F$; $R_F-(VM)_n-R_F$; R_F = fluoroalkyl group] can undergo the sol-gel reaction under alkaline conditions in the presence of low molecular weight aromatic compounds such as 1,1'-bi(2-naphthol) (BINOL) to give the corresponding oligomer/silica nanocomposites [$R_F-(VM-SiO_2)_n-R_F$] - encapsulated BINOL [9]. Interestingly, encapsulated BINOL can exhibit a nonflammable characteristic even after calcination at 800 °C, although the corresponding oligomer in the nanocomposites afford a usual flammable behavior under similar conditions [9]. This nonflammable characteristic is due to the formation of ammonium hexafluorosilicate in the composites based on the bond-strengthening effect in Si-F bond (129 kcal or 540 kJ/mol) [10] during the nanocomposite reactions. $R_F-(VM)_n-R_F$ oligomer also undergoes the sol-gel reaction under alkaline conditions to afford the corresponding fluorinated oligomer/silica nanoparticles [$R_F-(VM-SiO_2)_n-R_F$] [11]. The modified glass surface treated with the $R_F-(VM-SiO_2)_n-R_F$ oligomeric nanoparticles can exhibit a completely hydrophobic (superhydrophobic) characteristic (a water contact angle of 180°) with a non-wetting property against water droplet. [11] From the developmental viewpoint of new fluorinated polymers/inorganic nanocomposites, it is of particular interest to explore new fluorinated oligomers/inorganic nanocomposites by using not only silica particles but also other inorganic particles. Here we report that calcium silicide ($CaSi_2$) and talc fine particles can be applied to the nanocomposite reactions with $R_F-(VM)_n-R_F$ oligomer under alkaline conditions to give the expected $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ and /talc nanocomposites, respectively. Especially, we have found that these obtained $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ and /talc nanocomposites are applicable to the facile creation of the superoleophobic-superhydrophilic and superoleophilic-superhydrophobic surfaces. These results will be demonstrated in this conference.

2 RESULTS AND DISCUSSION

As shown in Scheme 1, $R_F-(VM)_n-R_F$ oligomer reacted with calcium silicide [$CaSi_2$] particles under alkaline conditions to give the corresponding $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites in good isolated yields.



Scheme 1: Preparation of $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites.

FE-SEM (Field Emission Scanning Electron Micrograph) measurements show the formation of the uniform $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ composite fine nanoparticles with mean diameter: 58 ~ 68 nm before and even after calcination at 800 °C. The formation of uniform nanocomposite fine particles indicates that the $CaSi_2$ particles should be effectively encapsulated into the fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica nanocomposite cores during the nanocomposite reactions with the corresponding oligomer under alkaline conditions to give the expected $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposite fine particles possessing a good dispersibility and stability toward a variety of organic media.

We have prepared the modified glasses treated with $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites. The contact angles of dodecane and water for these glass plates were measured by depositing a droplet of dodecane or water (2 μ l) on the modified glass surfaces (see Fig. 1).

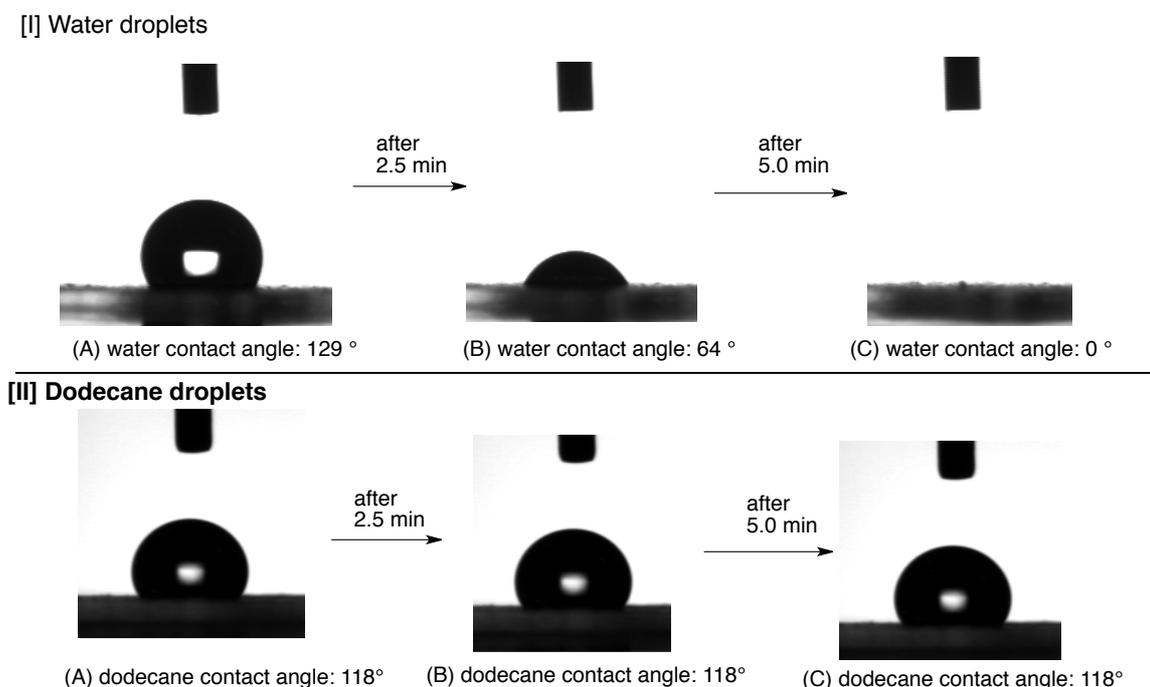


Figure 1: Charge coupled device camera images of the water and dodecane droplets on the modified glass surface treated with $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites [initial contact angle (A), contact angle after 2.5 min (B), and contact angle after 5.0 min (C)].

The contact angles of dodecane on the modified glass surfaces treated with the $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites showed large values: 118°, of whose value can exhibit superoleophobic characteristic imparted by fluoroalkyl segments in the composites. On the other hand, interestingly, a steep time dependence of water contact angle was observed in the $R_F-(VM-SiO_2)_n-R_F/CaSi_2$ nanocomposites. The water contact angles decreased smoothly from 129° to 0° over 5 min to give a superhydrophilicity on the modified surfaces.

This finding suggests that at the interface with water, hydrophobic fluoroalkyl segments

are replaced by the hydrophilic CaSi_2 particle surface, of whose parent particles can exhibit the water contact angle: 0° on the modified surface. It takes about only 5 min to replace the fluoroalkyl segments by the CaSi_2 units when the environment is changed from air to water.

The dodecane contact angle value on the parent polyester (PET) fabric swatch is 0° . However, the modified PET fabric swatch treated with the $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F/\text{CaSi}_2$ nanocomposites was also found to exhibit the dodecane and water contact angle values: 105° and 0° (The water contact angles decreased smoothly from 85° to 0° over 5 min.), respectively. This finding suggests that these modified surfaces can exhibit the superoleophobic-superhydrophilic characteristic. Thus, we tried to separate the mixture of oil (dodecane) and water (water was red-colored with Rhodamine B illustrated in Fig. 2) by using the modified PET fabric swatch as the liquid-liquid separation membranes, and the result was shown in Fig. 3.

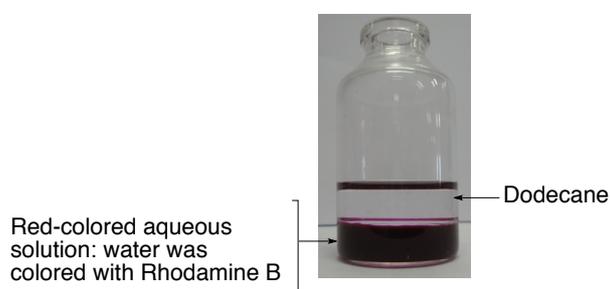


Figure 2: Photograph of the mixture of dodecane and red-colored aqueous solution.

Fig. 3 shows that the modified PET fabric swatch can be used for the effective separation of water and oil (dodecane), and only red-colored water has been removed under atmospheric pressure (see Fig. 3-(B)), although we cannot use the parent PET fabric swatch as the water – dodecane separation membrane under the similar conditions (see Fig. 3-(A)).

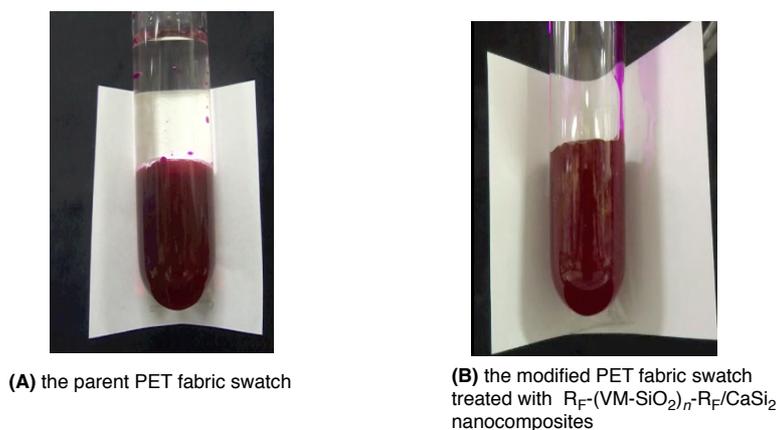
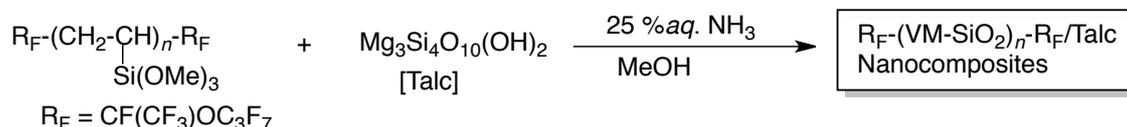


Figure 3: Separation of oil (dodecane)/water (red-colored aqueous solution) by using the parent PET fabric swatch (A) and the modified PET fabric swatch treated with $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F/\text{CaSi}_2$ nanocomposites (B) under atmospheric conditions.

Fluoroalkyl end-capped vinyltrimethoxysilane oligomer [$R_F-(VM)_n-R_F$] was also applied to the sol-gel reaction in the presence of talc particles under alkaline conditions to give the corresponding fluorinated oligomeric silica/Talc nanocomposites [$R_F-(VM-SiO_2)_n-R_F/Talc$] in excellent to moderate isolated yields (see Scheme 2).



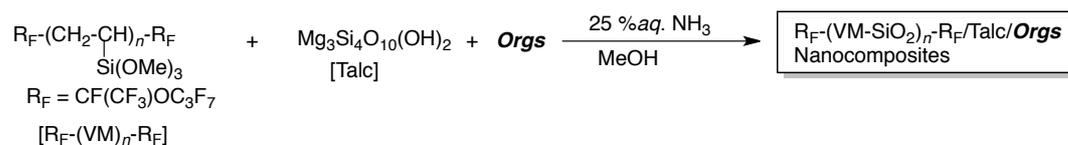
Scheme 2: Preparation of $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposites.

Next, we tried to encapsulate a variety of organic molecules (**Orgs**) into the $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposite cores, and the results are shown in Scheme 3.

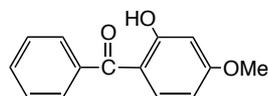
As shown in Scheme 3, encapsulation of **Orgs** into the $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposite cores were found to proceed smoothly to give the expected fluorinated nanocomposites–encapsulated **Orgs** [$R_F-(VM-SiO_2)_n-R_F/Talc/Orgs$]. This finding suggests that guest molecules such as HMB and BPA should be encapsulated into fluorinated nanocomposite cores through the Van der Waals interaction.

The $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposites–encapsulated HMB and BPA were found to exhibit the similar dispersibility and stability to that of the $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposites illustrated in Scheme 2.

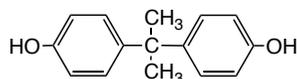
Here we tried to prepare the modified glasses treated with the $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposites and $R_F-(VM-SiO_2)_n-R_F/Talc/Orgs$ nanocomposites, and the contact angles of dodecane and water for these glass plates were measured by depositing a droplet of dodecane



Orgs:



[2-hydroxy-4-methoxybenzophenone (HMB)]



[bisphenol A (BPA)]

Scheme 3: Preparation of $R_F-(VM-SiO_2)_n-R_F/Talc/Orgs$ nanocomposites.

or water (2 μ l) on the modified glass surfaces. These results were shown in Table 1.

Run	Nanocomposites	dodecane	Contact angle (degrees)						
			dodecane				water		
			0 m	5 m	10 m	15 m	20 m	25 m	30 m
1	R _F -(VM) _n -R _F /Talc nanocomposites	43	180	- ^{a)}	-	-	-	-	-
	R _F -(VM-SiO ₂) _n -R _F oligomeric nanoparticles	48	180	- ^{a)}	-	-	-	-	-
2	R _F -(VM) _n -R _F /Talc/HMB nanocomposites	0	180	- ^{a)}	-	-	-	-	-
3	R _F -(VM) _n -R _F /Talc/BPA nanocomposites	0	180	- ^{a)}	-	-	-	-	-

Table 1: Contact angles of water and dodecane on the modified glass surfaces treated with R_F-(VM-SiO₂)_n-R_F/Talc nanocomposites and R_F-(VM-SiO₂)_n-R_F/Talc/**Orgs** nanocomposites.

As shown in Table 1, the R_F-(VM-SiO₂)_n-R_F/Talc nanocomposite (Run 1) can exhibit the similar contact angles values for dodecane (43°) and water (180°) to those (dodecane: 48° and water: 180°) of the parent R_F-(VM-SiO₂)_n-R_F oligomeric silica nanoparticles, although water and dodecane contact angle values on the modified glass surface treated with the parent talc particles were found to become 0° in each case. However, unexpectedly, the R_F-(VM-SiO₂)_n-R_F/Talc/HMB nanocomposites can give the superoleophilic (dodecane: 0°)-superhydrophobic (water: 180°) characteristic on the modified surface. A similar result was obtained in the R_F-(VM-SiO₂)_n-R_F/Talc/BPA nanocomposites as shown in Run 3. The creation of the superoleophilic surface at the interface with oil (dodecane) would be due to the smooth replacement from hydrophobic fluoroalkyl groups to the oleophilic HMB or BPA moiety in the composites. The oleophilic units in the composites are likely to be arranged regularly at the interface with oil. Especially, the fluoroalkyl groups in the composites can give the completely superhydrophobic characteristic through the flip-flop motion between oleophilic HMB or BPA moiety and the fluoroalkyl groups in the composites when the environment is changed from oil to water.

3 CONCLUSIONS

In this way, our present R_F-(VM-SiO₂)_n-R_F/CaSi₂ nanocomposites have high potential for the application to the excellent membrane materials for the oil/water separation, because of their exhibiting the superoleophobic-superhydrophilic characteristic on the modified surface. In addition, R_F-(VM-SiO₂)_n-R_F/Talc nanocomposites were prepared by the sol-gel reaction of

the corresponding oligomer in the presence of talc particles under alkaline conditions. The $R_F-(VM-SiO_2)_n-R_F/Talc/Orgs$ nanocomposites were also prepared under the similar sol-gel reactions in the presence of **Orgs**. $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposites were applied to the surface modification of glass to give the oleophobic-superhydrophobic characteristic on the modified surface. However, the encapsulations of **Orgs** into the $R_F-(VM-SiO_2)_n-R_F/Talc$ nanocomposite cores enable the modified glass surfaces to give the controlled wettabilities such as superoleophilic-superhydrophobic characteristic.

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